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L3: Entry 12 of 29

File: USPT

Feb 26, 1991

DOCUMENT-IDENTIFIER: US 4996271 A

TITLE: Method of manufacturing halogenated aromatic polysulfone compounds and the compounds so produced

Abstract Text (1):

Halogenation of Udel (trademark) and Radel (trademark) polysulfone occurs adily by electrophilic substitution. The reactive substitution position is situated ortho- to the aryl ether linkage in the Bisphenol-A portion of the repeat units. Halogenated polysulfones are obtained by reaction of the polymer with elemental halogen. Thus, a solution of Udel polysulfone in chloroform, treated with excess bromine at room temperature, gives dibrominated polysulfone III in high yield. The degree of substitution after 18-24 hours is typically 1.80 to 2.05 by bromine analysis. Similar results are obtained by reaction of the polymer with elemental chlorine. Lower degrees of substitution are obtained with shorter reaction times or using lesser amounts of halogen.

Brief Summary Text (3):

Polysulfones are high performance thermoplastics which have excellent mechanical properties, thermal and oxidative stability and high glass transition temperatures. A method of manufacturing the polymer starting materials is taught by R. N. Johnson and A. G. Farnham, U.S. Pat. No. 4,108,837 (1978). The introduction of functional groups into these polymers by chemical modification is well known to induce significant changes in physical properties. For example, the sulfonation of polysulfone I (n=1), taught by J. P. Quentin, U.S. Pat. No. 3,709,841 (1973), results in a polymer with increased hydrophilicity and glass transition temperature and which is useful for the fabrication of porous membranes.

Brief Summary Text (7):

There is a need for a method of manufacturing modified, aromatic polysulfone compounds or derivatives wherein there is greater scope for controlling the degree of halogenation and ease of preparation, thus resulting in products having a wider range of improved or modified chemical or physical properties such as, for example, glass transition temperature, hydrophilicity, hydrophobicity, solubility or chemical reactivity and which are processable into, for example, membranes, sheets, films, fibres or more rigid articles.

Brief Summary Text (9):

According to the present invention there is provided a method of manufacturing an aromatic polysulfone compound, comprising, (a) forming a solution of the polysulfone compound with halogenated solvent, the polysulfone compound having at least one repeating unit of the general formula, ##STR1## wherein n is one or zero, and when n is one, R.sub.1, and R.sub.2 each represent alkyl or aryl groups (b) adding sufficient halogen to the solvent to halogenate the polysulfone compound to the desired degree, so as to form a halogenated compound having repeat units of the general formula, ##STR2## wherein R.sub.1, R.sub.2 and n are as previously defined and at least one R.sub.3 per polymer chain is a halogen substitution of a hydrogen atom, (c) halogenated polysulfone compound from the solvent, and

Brief Summary Text (12):

The halogenated polysulfone separated from the solvent by, for example, solvent evaporation therefrom, or precipitation therefrom in a non-solvent liquid for the halogenated polysulfone.

Detailed Description Text (2):

In the following halogenation tests, chloroform was used as the solvent and the tests

were carried out at temperatures in the ranges specified. It will be self evident to persons skilled in the art that other halogenated solvents and temperatures will give similar results. Examples of other halogenated solvents are, dichloromethane, dibromomethane and tetrachloromethane. While the tests have shown that halogenation may be carried out at different temperatures, halogenation is adequately and conveniently carried out at room temperature. Polymers containing an average of two halogens per repeat unit are obtained by using a slight excess of halogen. Polymers with lower degrees of substitution of halogen are obtained by using lesser amounts of halogen or shorter reaction times.

Detailed Description Text (45):

Referring now to the drawings, FIG. 1 shows the 400 MHz NMR spectrum (aromatic region) of dibrominated polymer III (III, FIG. 1) compared with the unmodified polysulfone I (I, FIG. 1). The modification site in the Bisphenol-A portion of the polymer is shown by the largely unchanged downfield aryl-sulfone doublets. Protons ortho- to bromine appear as a meta-coupled doublet at  $\delta = 7.52$ . The unmodified polymer H-b doublet is replaced by a doublet of doublets at  $\delta = 7.16$  arising from ortho- and meta-coupling in the dibrominated polymer. Although the product had a lower viscosity, little or no degradation appeared to occur since the subsequently metalated/deuterated product VI (VI, FIG. 1) had a similar viscosity to polysulfone I.

Detailed Description Text (46):

The utility of dibrominated polymer III as a reactive polymer was demonstrated by the preparation of a simple dideuterated derivative by metalation. Dibrominated polysulfone III was metalated with n-butyllithium according to test VII and the lithiated intermediate was converted to dideuterated polymer VI by reaction with deuterium oxide. Both the bromine and the ortho-sulfone position are potentially reactive metalation sites; the first by simple metal-halogen exchange and the second by hetero-atom directed lithiation. A substantial amount of competition between these two reactions might be expected. However, the NMR spectrum of the dideuterated polymer VII also shown in FIG. 1 shows that metal-halogen exchange is the dominant reaction, with a minimal amount of ortho-lithiation evident in this derivative. The aryl sulfone doublets remain unaltered while the Bisphenol-A proton signals show dideuteration ortho- to oxygen by the H-b/h-e multiplet and the diminution of the doublet H-a in the NMR spectrum.

Detailed Description Text (49):

It is within the scope of the present invention to form the polysulfone compound to be halogenated into a solution with halogenated solvent, and then halogenate the polysulfone by adding both bromine and chlorine to the solution.

CLAIMS:

1. A method of manufacturing a halogenated aromatic polysulfone compound, comprising:
  - (a) forming a solution of the polysulfone compound with halogenated solvent, the polysulfone compound having repeating units of the general formula, ##STR11## wherein n is one or zero, and when n is one R.sub.1 and R.sub.2 each represent alkyl or aryl groups,
  - (b) adding sufficient halogen to the solvent to halogenate the polysulfone compound to the desired degree so as to form a halogenated compound having repeating units of the general formula, ##STR12## wherein R.sub.1, R.sub.2 and n are as previously defined and at least one R.sub.3 per polymer chain is a halogen substitution of a hydrogen atom, and
  - (c) separating the halogenated polysulfone compound from the solvent.
4. A method according to claim 1, wherein the halogenated polysulfone is separated from the solvent by evaporating the solvent.
5. A method according to claim 1, wherein the halogenated polysulfone is separated from the solvent by being precipitated therefrom in a non-solvent liquid for the halogenated polysulfone.

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L3: Entry 20 of 29

File: USPT

May 23, 1989

DOCUMENT IDENTIFIER: US 4833219 A

TITLE: Preparation of substituted polysulfones by metalation

Abstract Text (2):

(a) metalating (e.g. lithiating) a polysulfone, preferably dissolved in a solvent, containing repeating units of the formula: ##STR2## wherein R.sub.1, R.sub.2, R.sub.s and n are as defined above, so as to form a metalated (e.g. lithiated) polymer containing repeating units of the formula: ##STR3## wherein R.sub.1, R.sub.2, R.sub.s and n are as defined above, at least one M per polymer chain is metal 1 (e.g. lithium), with any remainder thereof being hydrogen; and

Brief Summary Text (3):

This invention relates to a process for preparing aromatic polysulfones, including polysulfone ionomers and other derivatives, involving the formation of novel metalated polymer intermediates. The polymers so produced exhibit improved or modified properties, which can be tailored to a desired end use by controlling the nature and degree of derivitization. The polysulfones so produced may, for example, be used for forming membranes, fibres, films, sheets and solid structures.

Brief Summary Text (5):

Polysulfones are a very stable class of polymers. However, the molecule generally lacks any useful functionality, rendering polysulfones useful only for applications in which their hydrophobic unreactive state is of advantage, for example in pipes and molded forms, as well as ultrafiltration and reverse osmosis membrane supports.

Brief Summary Text (9):

There is a need for a process which provides polysulfone derivatives having improved or modified chemical and physical properties, such as glass transition temperature, hydrophilicity, hydrophobicity, lipophilicity, dyeability, solubility or corrosion resistance, which may be suitable, for example, for forming membranes, sheets, films, fibres micro-spheres, or solid structures.

Brief Summary Text (23):

(a) dissolving or suspending the polysulfone in a solvent which is substantially unreactive with the metalating agent and the polysulfone,

Brief Summary Text (27):

The solvent may be tetrahydrofuran and in step (b) the solution may be cooled to a temperature in the range of -30.degree. C. to -70.degree. C.

Brief Summary Text (30):

In carrying out the process of the invention, the starting polymer is conveniently dissolved or suspended in a solvent, for example tetrahydrofuran, ether, hexane, dimethyl ethylene glycol or other suitable solvent. The solvent is not critical but should be substantially unreactive with the metalating agent and substrate. The reaction is carried out under anhydrous conditions and at a temperature of about 8.degree. C. or below, using a metalating agent, such as an organolithium compound, for example an alkyl or aryl lithium, particularly n-butyllithium, sec-butyllithium, iso-butyllithium, tert-butyllithium, methyllithium, ethyllithium, propyllithium, phenyllithium or lithium diisopropylamide, amongst others. Conveniently, the reaction will be carried out under an inert atmosphere, such as argon or nitrogen. The temperature of about 0.degree. C. appears to be an approximate upper limit for useful lithiation of most polymers, since above this temperature, while metalation probably takes place, competing reactions tend to occur, with formation of a precipitated insoluble product. Thus, for example, if the solution is cooled to a temperature no

greater than about 8.degree. C. and the metalating agent is added too rapidly, the heat of reaction causes the local temperature to rise and precipitate the polymer. Temperatures below -78.degree. C. (i.e. the temperature of dry ice/methanol) have not been tested, although it is believed likely that lithiation would still readily occur.

Brief Summary Text (31):

The upper limit of about 8.degree. C., to which the solution of the polymer is cooled may be different for different polymers and solvents, and, if additives are used, different additives. However, this upper limit can readily be determined for a particular use of the process by routine tests.

Brief Summary Text (34):

A large number of different electrophiles may be employed in this reaction step to form the desired derivatives, including aldehydes such as acetaldehyde, propionaldehyde, butyraldehyde and benzaldehyde; ketones such as dimethyl ketone, methyl ketone, diethyl ketone, diphenyl ketone and methyl phenyl ketone; isocyanates such as methyl or ethyl isocyanate, and phenyl isocyanate, thioisocyanates such as methyl thioisocyanate, ethyl thioisocyanate, phenyl thioisocyanate, disulfides such as dimethyl disulfide, diethyl disulfide, methyl ethyl disulfide and diphenyl disulfide; nitriles such as benzonitrile and acetonitrile; carbon dioxide; sulfur; sulfur dioxide; halogens such as chlorine, bromine and iodine; halogen-containing compounds such as alkyl halides, e.g. iodomethane, iodoethane, chloromethane, chloroethane, bromomethane and bromoethane, aryl alkyl halides, e.g. benzyl chloride and bromide and allyl halides, e.g. allyl iodide and allyl bromide; epoxides such as ethylene oxides and propylene oxide; amides such as dimethylacetamide; organometallic halides such as chlorotrimethyl tin, chlorotrimethyl germane and chlorotrimethyl silane; metallic halides such as silver bromide or cuprous bromide and nonmetallic halides such as chlorodiphenylphosphine. These compounds can be added alone, or as solutions in suitable unreactive solvents.

Brief Summary Text (36):

A particularly preferred group of product compounds of the process of the invention are the carboxylate-type polysulfone polysulfone ionomers which find use as membranes in electrolytic cells, as ion exchange membranes and in ion exchange columns, namely compounds of formula I wherein at least one of the groups R per polymer molecule represents carboxyl, carboxylic ester, or --COOM', wherein M' is a metal or ammonium ion, particularly those in which about 0.01 to 1 of the groups R per repeating unit represent carboxyl or --COOLi, and the remaining group R represents hydrogen.

Brief Summary Text (37):

However, a diverse range of useful products of the process and falling within formula I can be obtained by virtue of the high reactivity of the metalated polymer carbanion intermediate with a large number of electrophile, such as aldehydes, ketones, isocyanates, disulfides, nitriles, sulfur, sulfur dioxide, halogens and halogen-containing molecules, epoxides, amides; aldimines, thioisocyanates, anhydrides, alkyl halides, aryl-alkyl halides, thiiranes, nitrogen oxides, metal halides, non-metal halides, organometallic halides and borates among others. For example, the reaction of a carbanion with an aldehyde or ketone gives an alcohol which increases the hydrophilicity and wettability of the polymer. This property is very useful in membrane and separator science where the hydrophilicity of a polymer can be adjusted to give optimum results.

Brief Summary Text (47):

However, test results have indicated that reaction conditions, i.e. temperature, solvent used, concentration of reactants and rate of addition of the lithiating agent, rate of heat removal of heat during the reaction, among other things, should readily be determined by routine tests which would favour monolithiation.

Brief Summary Text (58):

In another test Radel.RTM. Polysulfone which contains repeating units of the formula: ##STR22## was lithiated. The difference in structure lies in the presence of an aryl-aryl linkage instead of the presence of an isopropylidene linkage giving a Bisphenol-A structure, thereby making Radel Polysulfone a completely aromatic polymer.

Brief Summary Text (62):

For example, the reaction of a metalated polysulfone with an aldehyde or ketone was found to give an alcohol which greatly increases the hydrophilicity and wettability of the polymer. This property is very useful in membrane and separator science where the hydrophilicity of a polymer can be adjusted to give optimum results.

Brief Summary Text (66):

The solvent, in this case tetrahydrofuran (THF), was dried by refluxing over lithium aluminum hydride (LAH) and under argon for at least 1 hour and then freshly distilled for each reaction. Again this is not a limiting method of operation, but an indication that dry tetrahydrofuran is required for the reaction, otherwise the alkyl lithium will first react with any moisture present.

Brief Summary Text (69):

The derivatized polymers were recovered by precipitation into isopropanol or methanol or any other suitable non-solvent, filtered and then treated with water or alcohol. The polymers were dried in a vacuum or convection oven at 120.degree. C. overnight.

Detailed Description Text (92):

A solution of Benzophenone in THF was added slowly to a mechanically stirred solution of monolithiated Udel Polysulfone (0.05 mol) in THF (750 mL) at -70.degree. C. After 5 minutes a thick translucent gel formed which was stirred for 2 hours at -30.degree. C. and then precipitated into alcohol, washed in dilute hydrochloric acid, water and finally in alcohol (31.2 g, 91% yield). A transparent membrane prepared for IR analysis had an absorption band at 3410 cm.<sup>sup.-1</sup> corresponding to OH stretch.

## CLAIMS:

7. A process according to claim 1, wherein the polysulfone is lithiated by,

(a) dissolving the polysulfone in a solvent which is substantially unreactive with the metalating agent and the polysulfone,

(b) cooling the solution to a temperature no greater than about 8.degree. C.,

(c) adding the metalating agent under anhydrous conditions while continuing the cooling of the cooled solution to the said temperature, and

(d) allowing the metalating agent to react with the polysulfone.

8. A process according to claim 7, wherein the solvent is tetrahydrofuran.

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<u>L3</u>	L2 and solvent and non-solvent	29	<u>L3</u>
<u>L2</u>	L1 and membrane	155	<u>L2</u>
<u>L1</u>	"bisphenol a" same polysulfone	745	<u>L1</u>

END OF SEARCH HISTORY